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**20. ABSTRACT (Continue on reverse side if necessary and identify by block number)**

Alkali halide molecules dissociated by shock waves in gases exhibit population distributions far from equilibrium. The kinetics of the subsequent chemical relaxation have been worked out and the rate coefficients have been determined for many of these ionic molecules. In some cases, the nonequilibrium populations are highly inverted, and in at least two systems, the inverted population has been used to produce light amplification (lasing action) with spectral lines in the visible region.

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THERMALLY-PRODUCED POPULATION INVERSIONS AND THEIR CONSEQUENCES

FINAL TECHNICAL REPORT

R. Stephen Berry, Principal Investigator

30 May, 1980

U.S. ARMY RESEARCH OFFICE

GRANT DAAG29-77-G-0080

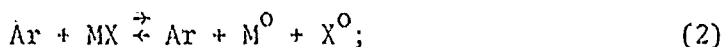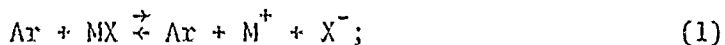The University of Chicago
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This research has been the exploration and exploitation of observations made first by us,[1,2] under ARO support, and then by others,[3-5] that when gaseous alkali halide molecules are dissociated by collisions behind shock waves, the population of dissociated species has a distribution far from equilibrium. The salts of rubidium and cesium, and some of the salts of potassium and even sodium, have their populations inverted in the sense that the fraction of molecules dissociating to ions, relative to the fraction dissociating to neutral atoms in their lower-energy ground states, far exceeds the fraction corresponding to thermal equilibrium at infinite temperature. The research carried out under this Grant has been directed toward a) elucidating the kinetics of chemical relaxation of these systems from their distributions immediately following the shock-induced heating to equilibrium, and b) making use of the inverted populations to generate processes of interest such as lasing action. The research consisted of two kinds of shock-tube experiments, plus interpretive work in the form of modeling calculations and theoretical studies. The experiments were systematic kinetic studies corresponding to a) above, and exploratory spectroscopic investigations of the possibilities of lasing action or other interesting light emission phenomena, under the rubric of b), above.

The kinetic studies were begun under a previous Grant from the Army Research Office and have now been completed. The results, which constitute the doctoral theses of Richard Milstein and Joseph Weber, provide a quantitative picture of the relaxation processes for RbCl, RbBr, RbI, CsCl, CsBr, CsI, and, slightly less extensively, NaCl and KBr. The model is based on the following set of reactions:

(Let M = alkali, X = halogen, * = electronic excitation)

$$Ar + MX \overset{\rightarrow}{\underset{\leftarrow}{}} Ar + M^+ + X^-; \tag{1}$$

$$Ar + MX \overset{\rightarrow}{\underset{\leftarrow}{}} Ar + M^O + X^O; \tag{2}$$

$$Ar + X^- \overset{\rightarrow}{\underset{\leftarrow}{}} Ar + X + e; \tag{3}$$

$$M^O + X^O \overset{\rightarrow}{\underset{\leftarrow}{}} M^+ + X^-; \tag{4}$$

$$M^O + e \overset{\rightarrow}{\underset{\leftarrow}{}} M^+ + 2e; \tag{5}$$

$$X^- + e \overset{\rightarrow}{\underset{\leftarrow}{}} X^O + 2e; \tag{6}$$

$$MX + e \overset{\rightarrow}{\underset{\leftarrow}{}} M + X^-; \tag{7}$$

$$MX + e \overset{\rightarrow}{\underset{\leftarrow}{}} M + X + e. \tag{8}$$

At higher temperatures, the model also included

$$M^* + X \overset{\rightarrow}{\underset{\leftarrow}{}} M^+ + X^- \tag{9}$$

and
$$M^* \rightarrow M + h\nu. \tag{10}$$

We investigated the importance of ionized halogen and ionized argon, and found they are unimportant under the conditions of our experiments.

The temperature range of the studies was about 2000-7000K. The kinetics experiments were carried out by monitoring absorption spectra, either photo-metrically or photographically, as functions of time. The species monitored were the alkali atoms, the halide ions and the diatomic molecules. The kinetic model contains six species (except at high temperatures, where it includes $M^*$ as a seventh). Moreover there are two equations for mass conservation--one for M and one for X--and one for charge neutrality. Hence in principle each system is completely determined. Moreover the reactions were often followed to equilibrium, where the thermodynamic

equilibrium constants provide an additional set of constraints; and finally, the rate coefficients for processes common to more than one salt, such as $Ar + Br^- \rightarrow Ar + Br + e$, must be consistent from one salt to another. Consequently the reaction system is highly overdetermined.

In practice this overdetermination is not quite so complete because of uncertainties, for example, in the temperature dependencies of molecular absorption coefficients, or of the precise corrections to be made when spectral lines are not thin. Nevertheless the net result is a rather satisfying picture in which rate coefficients for reactions (1)-(5) have been determined, and in which upper bounds have been found for reactions (6)-(8) which say that they are not important in our systems. Moreover the rate coefficients for reactions (1)-(5) have been measured over temperature ranges long enough to permit us to fit them to phenomenological forms such as Arrhenius expressions and to determine the phenomenological parameters. In cases where our results may be compared with those of other flame or shock tube studies, the agreement is quite good.[5,6] The shock-tube results from three laboratories for Reaction (3), $Ar + X^- \rightarrow Ar + X + e$, are quite consistent. The results for reaction (4) are consistent with those from flame studies,[7] when one takes into account that the flame kinetics work distinguished $M^o + X^o \rightarrow M^+ + X^-$ from $M^o + X^o + Ar \rightarrow M^+ + X^- + Ar$ but our work did not. The results from the shock tube studies, while self-consistent, are not all in good agreement with flame studies, e.g. for reaction (1), and there has been a well-recognized difference between the shock tube studies and molecular beam studies for reaction (3). Our results have been presented in preliminary form in Mandl's review[5] and summarized

in part by this writer;[6] the latter reference also states the present
situation regarding the discrepant rates. The results are available in
detail in the theses of Milstein[8] and Weber[9] (which, at the time of this
writing, is still in draft form), and will be published soon after Weber's
thesis is accepted.

The second part of the experimental research involved combining knowl-
edge of the inverted populations, together with the knowledge that near-
resonant ion-ion neutralization has a very large cross section, to try to
generate large populations of atoms in excited electronic states, by the
process (9) in reverse, $M^+ + X^- \rightarrow M^* + X$. This work was successful when
Na was used as M and I was used as X. The results were sometimes intense
bursts of light from the yellow NaD line and sometimes nonsinusoidal but
oscillatory emission of the same light.[10] These processes have been modeled
by H-T Wang in studies carried out under the ARO Grant, and will be published.
They appear to be the consequences of the nonlinearity of the kinetic
system (1)-(5), (9), (10), especially the autocatalytic reaction (5).

Light amplification in ion-ion neutralization had been observed in
the far-from-resonant case of $Na^+ + H^-$ by Tibilov and Shukhtin.[11] We
found amplification in the blue wings of the NaD line and several Rb lines
which we attributed to $NaAr^+ + I^- \rightarrow NaAr^* + I$ and $NaAr^* \rightarrow Na + Ar + h\nu$ and
to the corresponding processes with Rb.[12] The electron transfer step in
our system is very nearly resonant. Research subsequent to the Grant dis-
cussed here is pursuing these phenomena in more detail.

During some theoretical studies aimed at understanding the reactions,
expecially $M^+ + X^- \rightarrow M^* + X$ and $MAr^+ + X^- \rightarrow MAr^* + X$, H.-T. Wang was able

to extend many of the ideas of quantum defect theory to states of atoms with two valence electrons. This work will be published in due cours .

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